

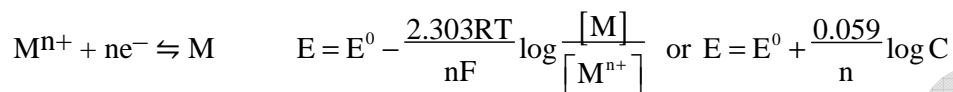
## ELECTRO CHEMISTRY

## NERNST EQUATION, BATTERIES CORROSION, PASSIVITY

## I: Nernst equation:

Nernst equation gives the dependence of the electrode potential on the concentration of ion with which the electrode is reversible. This equation holds good for reversible electrodes.

- a) For metal electrodes, the half-cell reaction is

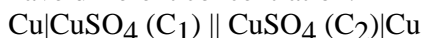


- b) For non - metal electrodes, the half cell reaction is  $A + ne^{-} \rightleftharpoons A^{n-}$

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[A^{n-}]}{[A]} \quad \text{or} \quad E = E^0 - \frac{0.059}{n} \log C$$

For H electrode  $E = -0.059 \text{ pH}$

- c) Concentration cell is galvanic cell in which both the electrodes are of same type but the electrolytes have different concentration.



The cell potential of the concentration cell can be calculated by

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

$$\text{At } 298\text{K, } E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

- d) When the cell reaction is in equilibrium, the cell EMF (E) is zero. So the Nernst Equation is

$$E^0 = \frac{2.303RT}{nF} \log K_c \quad (\text{or}) \quad E^0 = \frac{0.0591}{n} \log K_c$$

- e) FOR HYDROGEN ELECTRODE:  $2H^+ + 2e^{-} \rightarrow H_2$  (Patm.),  $E_{\text{RP}} = E_{\text{RP}}^0 - \frac{0.059}{n} \log \frac{P_{H_2}}{[H^+]^2}$

- f) FOR ELECTRODE CONCENTRATION CELLS:-

The two electrodes of different concentration are dipped in the same solution of electrolyte.

$$\text{Eg1 } Pt, H_{2(P_1)} / H^+ / H_{2(P_2)}, Pt, \quad E_{\text{cell}} = \frac{0.059}{n} \log \frac{P_1}{P_2}$$

$$\text{Eg2 } Pt, Cl_{2(P_1)} / Cl^- / Cl_{2(P_2)}, Pt, \quad E_{\text{cell}} = \frac{0.059}{n} \log \frac{P_2}{P_1}$$

- g)  $\text{Emf of cell} = E^0_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$

## II; Cell potential – Gibbs Energy:

- I. The change in free energy is represented by  $\Delta G$ .
- ii. For spontaneous reaction,  $\Delta G$  will have negative value ( $\Delta G = -ve$ )
- iii. Electrical work done in one second = Electrical potential  $\times$  total charge passed.
- iv. To obtain maximum work from a galvanic cell, the charge has to be passed reversibly.
- V. The reversible work done by a galvanic cell = decrease in its free energy.  
 $W_{\max} = -\Delta G$  (or)  $\Delta G = -W_{\max}$
- Vi. When no current is drawn from the cell, the EMF of the cell is  $E$ , the amount of charge passed is  $nF$  ( $n$  = no of electrons and  $F$  = Faraday) then  $\Delta G = -nFE$
- Vii. If the activity of reacting species is unity, then  $E = E^0$ , then we can have  
 $\Delta G^0 = -nFE^0$   
 From standard free energy, the equilibrium constant can be calculated  
 $\Delta G^0 = -RT \ln K_c$  or  $\Delta G^0 = -2.303RT \log K_c$
- Viii: If two half cell reactions having electrode potential  $E_1^0$  and  $E_2^0$  are combined to give a third half cell reaction having an electrode potential  $E_3^0$  then  $\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0$   
 i.e  $-n_3FE_3^0 = -n_1FE_1^0 - n_2FE_2^0$  or  $E_3^0 = \frac{n_1E_1^0 + n_2E_2^0}{n_3}$   
 \* If number of electrons involved are equal then  $E_3^0 = E_1^0 + E_2^0$

## III.SOME COMMERCIAL CELLS AND BATTERIES:-

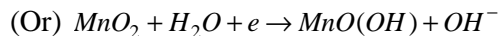
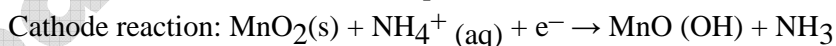
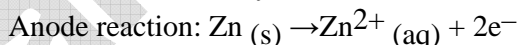
- i) The electrochemical cells can be used to generate electricity.
- ii) The word battery is used for two (or) more galvanic cells generally connected in series.
- iii) There are two types of commercial cells:

### (a) Primary cells:-

- i) It is an electrochemical cell which acts as a source of electrical energy without being previously charged up by an electric current from an external source of current.
- ii) In which electrode reactions cannot be reversed by external source.
- iii) These are not chargeable.
- iv) Examples of this type is dry cell (or) Leclanche cell, voltaic cell.

### I .Dry cell or Leclanche cell

Dry cell consists of a zinc container which acts as anode and graphite as cathode rod surrounded by powdered manganese dioxide and carbon. The Zinc electrode is in contact with paste of ammonium chloride and zinc chloride. The paste,  $C + MnO_2$  and  $NH_4Cl + ZnCl_2$  are separated by a porous sheet. The zinc vessel is surrounded by card board. The zinc vessel is sealed with pitch. The following reactions occur in dry cell,.



Zn is reductant &  $MnO_2$  is oxidant and acts as depolarizer.

The secondary reactions taking place in dry cell are  $NH_4Cl + OH^- \rightarrow NH_3 + Cl^- + H_2O$ ,



Ammonia produced in the reaction forms a complex,  $[Zn(NH_3)_4]^{2+}$ . The potential of the cell is nearly 1.5V.

**ii. Mercury cell:** It is used for low current devices

Anode: ZnHg

Cathode: paste of HgO & Carbon

Electrolyte: paste of KOH & ZnO

Anode reaction,  $\text{ZnHg} + 2\text{OH}^- \rightarrow \text{ZnO}_{(s)} + \text{H}_2\text{O} + \text{Hg}_{(l)} + 2e^-$

Cathode reaction,  $\text{HgO} + \text{H}_2\text{O} + 2e^- \rightarrow \text{Hg}_{(l)} + 2\text{OH}^-$

Zn is reductant and HgO is oxidant

Overall cell reaction is  $\text{Zn} + \text{HgO}_{(s)} \rightarrow \text{ZnO}_{(s)} + \text{Hg}_{(l)}$

Overall reaction does not involve any ion.

Cell potential remains constant during its life. Cell potential – 1.35 volt.

**(b) Secondary cells:-**

i) Electrical energy from an external source is first converted into chemical energy (Electrolysis) and when the source is removed then the cell is made to operate in the reverse direction.

ii) Secondary cells are those which can be rechargeable and used again and again.

iii) These are designed to convert the energy from combustion of fuel such as  $\text{H}_2$ , CO,  $\text{CH}_4$  etc directly into electrical energy.

iv) The common examples are hydrogen-oxygen fuel cell, Hydrocarbon fuel cell Ni-Cd cell, Lead accumulator, Li-ion battery.

v) Acid storage cell is Lead accumulator and Alkali storage cell is Edison Battery

Lead storage battery”: It is used in automobiles & invertors.

Anode: Lead grids of filled with spongy lead

Cathode: Lead grids of filled with  $\text{PbO}_2$

Cathode & anode are arranged alternately. Cathode and anode are separated by thin fibre glass sheets

Electrolyte: 38% (by weight) solution of  $\text{H}_2\text{SO}_4$

Anode reaction,  $\text{Pb} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2e^-$

Cathode reaction,  $\text{PbO}_2 + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+ + 2e^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

Overall cell reaction,

$\text{Pb}_{(s)} + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

During working of cell,  $\text{H}_2\text{SO}_4$  is used up (during discharge)

During charging of battery, cell reactions are reversed. i.e.,  $\text{PbSO}_4$  on anode is converted to  $\text{Pb}_{(s)}$  and

$\text{PbSO}_4$  on cathode is converted to  $\text{PbO}_2(\text{s})$

At anode -  $\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2e^-$

At cathode  $\text{PbSO}_4(\text{s}) + 2e^- \rightarrow \text{Pb}_{(s)} + \text{SO}_4^{2-}(\text{aq})$

Lead sulphate accumulated at cathode and anode is converted into lead and lead dioxide respectively.

Charging and discharging of lead storage battery is known as double sulphation. The voltage increases with the concentration of electrolyte. The voltage varies from 1.88V

(5%  $\text{H}_2\text{SO}_4$ ) to 2.15V (40%  $\text{H}_2\text{SO}_4$ ).

**Nickel - Cadmium cell:** It has longer life than lead storage battery but more expensive. In this

Anode – Cd (s)

Cathode – Ni (OH)<sub>3</sub> (s)

Electrolyte – Moist NaOH (or) KOH

Cell potential 1.4 volt

Cell reaction:  $\text{Cd}_{(s)} + 2\text{Ni}(\text{OH})_{3(s)} \rightarrow \text{CdO}_{(s)} + 2\text{Ni}(\text{OH})_{2(s)} + \text{H}_2\text{O}(\text{l})$

Cd – reductant & Ni (OH)<sub>3</sub> – oxidant

#### IV: FUEL CELLS:

Fuel Cells are Galvanic cells that convert energy of combustion of fuels like hydrogen, methane, and methanol etc., directly into electrical energy are called fuel cells.

1. Fuel cells may be liquid fuel cells (or) gas fuel cells.

i. In liquid fuel cells  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{HCHO}$ ,  $\text{N}_2\text{H}_4$  are used as fuels.

ii. In gas fuel cells -  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$  etc. are used as fuels.

2. Fuel cells i) working below 100°C are low temperature cells.

ii) Working between 100-250°C are medium temperature cells.

iii) Working above 500°C are high temperature cells.

3.  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ , air,  $\text{O}_2$  etc. are used as oxidants.

4. Pt, Porous PVC, PTFE coated with Ag are used as electrodes.

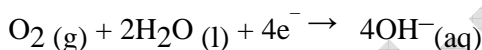
5. In biochemical cells organic compounds disintegrated by micro organisms. These are in use now a day.

a)  $\text{H}_2$  -  $\text{O}_2$  FUEL CELL: [The cell used to supply electrical power in the Apollo space program].

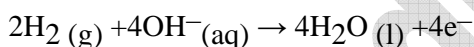
Electrodes: Porous carbon electrodes with catalysts like finely divided platinum or palladium.

Electrolytes:  $\text{H}_2$  and  $\text{O}_2$  are bubbled through concentrated aqueous NaOH solution.

Cathode Reaction:



Anode Reaction,



Overall reaction –  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

The cell runs continuously as long as reactants are supplied. Efficiency of fuel cell is about 70% and

Fuel cells are pollution free

General representation of fuel cell: Fuel/electrode/ electrolyte/ electrode / oxidant

#### b) HYDROCARBON-OXYGEN FUEL CELL:

Hydrocarbons are burned in oxygen at high temperature to get large amount of electrical energy.

Air freed from impurities (or) pure oxygen is oxidant.

Aq. KOH is used as electrolyte.

Pt electrodes are used.

$\text{H}_3\text{PO}_4$  is used as electrolyte if hydrocarbon is burned. It is because the obtained  $\text{CO}_2$  in combustion is absorbed by Aq. KOH.

#### V. Corrosion

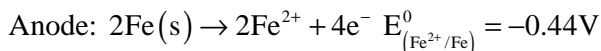
The natural tendency of conversion of a metal into its mineral compound form on interaction with the environment (Polluted air, water, associated other Metals etc) is known as corrosion

Ex : Iron converts itself into its oxide (  $\text{Fe}_2\text{O}_3$  - haematite), Copper converts itself into its carbonate (  $\text{CaCO}_3 \cdot \text{Cu}(\text{OH})_2$  - Malachite), Silver converts itself into its sulphide (  $\text{Ag}_2\text{S}$  - horn silver).

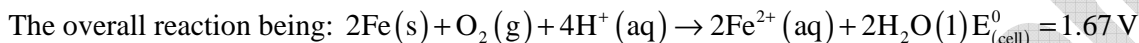
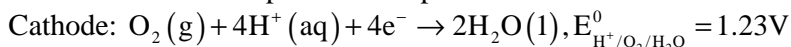
\*Corrosion in case of iron is known as rusting and in case of silver is known as tarnishing.

Mechanism In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides.

Corrosion of iron (commonly known as rusting) occurs in presence of water and air. At a particular spot (figure given above) of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction.



Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of  $\text{H}^+$ , which is believed to be available from  $\text{H}_2\text{CO}_3$  formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere. This spot behaves as cathode with the reaction.



The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide, i.e.  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

The process of corrosion may be chemical (or) electro chemical in nature

The anodic dissolution of a metal under the conditions of corrosion is known as electrochemical corrosion  $M \rightarrow M^{n+} + ne^-$

Corrosion occurs if the environmental conditions of the metal favour the formation of an voltaic cell with the metal acting as anode

Electro - chemical corrosion is basically of two types

- 1) Hydrogen evolution type
- 2) Differential oxygenation type

### 1. HYDROGEN EVOLUTION TYPE:

i. This type of corrosion is exhibited by metals which can displace  $\text{H}_2$  gas from aqueous solution.

ii. This happens if the electrode potential of the metal under the conditions of corrosion is more negative than that of the hydrogen electrode under the given conditions.

iii. The hydrogen electrode potential depends on the nature of the metal used as the

Cathode and the  $\text{P}^{\text{H}}$  of the solution. It is almost zero (0V) in 1M acid solution, if the cathode metal is platinised platinum (Black Platinum)

It is about 0.8 V if the cathode metal is Hg

For other Metals the value lies in between these two values (0 to 0.8V)

This type of corrosion depends upon

- 1) The  $\text{P}^{\text{H}}$  of the medium
- 2) Chemical nature of the metal under going corrosion

Eg. Pure zinc does not corrode in salt solutions but in the presence of Cu as impurity Zn corrodes.

Zn corrodes in 2M acid but not in neutral salt solution

### 2. Differential oxygenation corrosion

i. This type of corrosion occurs if  $\text{O}_2$  concentration is not uniformly distributed on the surface of the metal

ii. Corrosion of the metal generally occurs at the point where  $\text{O}_2$  concentration is less

iii. The portion of the metal with access to high concentration of  $\text{O}_2$  functions as cathode and with access to low concentration of  $\text{O}_2$  functions as anode. Hence, the metal with differential oxygenation acts as a galvanic cell

**Ex :** When an iron rod is immersed in NaCl solution the immersed part is corroded due to less oxygenation of the surface of the metal.

Factors that promote electrochemical corrosion

i. The nature of the impurity metal with which the metal under consideration is associated

For Ex: Cu favours corrosion of Zn. because Zn is more anodic than copper

Zn disfavors corrosion of 'Fe' (Galvanization)

ii. The concentration of  $O_2$  in contact with the surface of the metal

For Ex: Metal rod half immersed in aqueous salt solution gets corroded at the surface not exposed to  $O_2$ ,

i.e., the immersed part of the Metal gets easily corroded

iii. Highly conducting solutions favour rapid corrosion Prevention of Corrosion

The main principle underlying the methods of prevention of corrosion is to separate the metal (or) isolate the metal from the environment is achieved by different ways. They are

(a) Painting

(b) Alloying (galvanisation)

(c) To prevent as far as possible the contact of the metal surface with good electrical conducting media

(d) Covering by some chemicals like bisphenol.

(e) Cover the surface by other metals (Sn, Zn etc) that are inert (or) react to save the object.

(f) Sacrificial electrode of another metal (like Mg, Zn, etc) which corrodes itself but saves the object.

VI: Passivity

The phenomenon of a metal reaching a stage of non-reactive state in its reaction with concentrated acids may be called passivity.

Iron group of metals and some other transition metals are rendered passive with concentrated acids.

Passivity of a metal can be classified into following three types.

#### **i. Chemical passivity**

Non - reactivity of metals after initial reaction with conc  $HNO_3$  is called chemical passivity

Eg: If iron is dipped in conc  $HNO_3$  it is attacked for some time and after becomes inactive.

Passive iron don't dissolve in dil  $HNO_3$  and iron don't displace Ag from  $AgNO_3$

Co, Ni, Cr can also become passive. Air can also cause passivity to Fe, Cr, Mo, and W&V

#### **ii. Mechanical Passivity**

In some cases dissolution of metal stops due to visible oxide film formation, this is mechanical passivity

Eg:  $PbO_2$  on  $Pb$

Fe, Co, Ni, Mn also exhibits this type of passivity

#### **iii. Electrochemical passivity:**

Metal with more -ve SRP functions as anode in cell

Generally Fe, Ni, Co functions as anode. They dissolve as  $M \rightarrow M^{+n} + ne^-$

At particular stage anode stops dissolving due to formation of invisible metal oxide film, this phenomenon is called electro - chemical passivity.